

# Molecular dynamics simulations of aqueous urea solutions: Study of dimer stability and solution structure, and calculation of the total nitrogen radial distribution function $G_N(r)$

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Molecular dynamics simulations have been performed in order to study the structure of two molal urea solutions in  $D_2O$ . Several initial dimer configurations were considered for an adequate sampling of phase space. Eventually all of them appeared to be unstable, when system size and periodic boundary conditions are chosen properly, even after a very careful equilibration. The total nitrogen scattering function  $G_N(r)$ , calculated from these simulations, is in good agreement with neutron scattering experiments when both intra- and intermolecular correlations are considered and the experimental truncation ripples are introduced by a Fourier transform of  $G_N(r)$  back and forth. The simple pair potential model that we used gives results in good agreement with experiments and with a much more involved potential model, recently described in the literature [J. Chem. Phys. **95**, 8419 (1991)].

## I. INTRODUCTION

Aqueous urea solutions have been thoroughly investigated because of the remarkable fact that urea increases the solubility of hydrocarbons in water,<sup>1</sup> induces protein denaturation,<sup>2</sup> and inhibits micellar aggregation.<sup>3</sup> Several models have been proposed to explain these and other thermodynamic properties of urea solutions. Two indirect mechanisms concentrate on the urea solution itself, rather than on direct interactions of urea and water with the solute:

(1) The first model, strongly advocated by Frank and Franks,<sup>4</sup> introduces the concept of urea acting as a water "structure breaker" (FF model). Pure water is supposed to consist of structured, ice-like domains and structureless, more dense domains. Urea molecules then tend to shift the equilibrium between these two domains in favor of the structureless domains.

(2) The second model was proposed by Schellman<sup>5(a)</sup> and refined by Kreschek and Scheraga<sup>5(b)</sup> and by Stokes<sup>5(c)</sup> (SKSS model). These authors assume that urea-urea interactions play an important role in solvation phenomena in aqueous urea solutions by the formation of urea dimers and oligomers.

The validity of these models has been investigated by a number of molecular dynamics simulations. Kuharski and Rossky<sup>6</sup> have objected to the mechanism of urea acting as a breaker of water structure. Neither did Tanaka *et al.*<sup>7</sup> find evidence that urea destroys the water structure, but they stressed the importance of urea self-association in solution. Cristinziano *et al.*,<sup>8</sup> however, using  $NpT$  instead of  $NVT$  simulations to allow volume relaxations for urea-urea H bond rearrangements, found the dimer to be only partially stable in aqueous solution.

To our knowledge only one experiment has been reported yielding detailed information about the structure of aqueous urea solution on a molecular level. Some years ago Finney and Turner<sup>9</sup> performed neutron scattering experiments to measure the total nitrogen-centered pair correla-

tion function  $G_N(r)$  of a two molal urea solution in  $D_2O$ . They argue that the experimental cutoff of the scattering vector is large enough in order that the peaks and oscillatory structure represent real features of  $G_N(r)$ . Comparing their results to the broad and featureless  $G_N(r)$  from all available computer simulations (e.g., Tanaka *et al.*<sup>7</sup>), they conclude that none of the potential functions used in simulations is adequate to model the interactions in aqueous urea solutions. Very recently Åstrand *et al.*<sup>10</sup> developed a sophisticated polarizable model for the urea-water potential: nevertheless MD simulations using this potential fail to reproduce the experimental  $G_N(r)$  and show the same broad and featureless results as before. As a reason for this discrepancy they suggest the presence of urea dimers in the real solution, while these were manifestly absent in their simulated solution box, containing only one urea monomer.

Recently we have published two molecular studies on the morphology of urea crystals grown from the vapor<sup>11</sup> and from aqueous solution.<sup>12</sup> In this paper we aim at two goals:

—First we want to investigate the quality of the potentials that we have used in our previous work. To this end we have calculated several atom-atom radial distribution functions describing the structure of a two molal urea solution. We shall present the results in Sec. III A and compare them to the results of Åstrand *et al.*<sup>10</sup> In Sec. III C we will demonstrate that our  $G_N(r)$  qualitatively resembles the experimental  $G_N(r)$  after we have incorporated the effects of intramolecular correlations and the experimental cutoff, by performing a Fourier transformation of the simulated  $G_N(r)$ , followed by an inverse transformation up to the experimental truncation point.

—Second we want to investigate the presence of urea dimers in the solution. Their presence is important not only for the explanation of solvation phenomena in aqueous urea solutions, but also for the calculation of the morphology of urea crystals grown from aqueous solution.

Moreover it was supposed by Åstrand *et al.*<sup>10</sup> that the difference between the calculated and experimental  $G_N(r)$  should be attributed to the presence of dimers. In Sec. III B we will present our results and conclude that the presence of urea dimers is very unlikely.

## II. MOLECULAR DYNAMICS SIMULATIONS

Our molecular dynamics simulations were performed using the GROMOS<sup>13</sup> package. In order to reproduce the system used by Finney and Turner, all simulations were performed in a two molal solution of deuterated urea in D<sub>2</sub>O. For D<sub>2</sub>O the SPC/E (extended simple point charge model) potential<sup>14</sup> was used. The force field for urea was constructed<sup>12</sup> from the HHL (Hagler, Huler and Lifson)<sup>15</sup> potential for nonbonded interactions and GROMOS covalent parameters.<sup>16</sup> Covalent bond distances were constrained by means of the SHAKE algorithm,<sup>17</sup> allowing an integration time step of 2 fs.

Since one of our goals is to study the stability of urea dimers in solution, an adequate sampling of the phase space was important. If at the same time one wants to avoid unreasonably long running times, this can only be achieved by choosing several different starting configurations including one or more of the most probable dimers. Therefore we performed two simulations:

### A. Urea monomer in solution

From a large D<sub>2</sub>O cluster consisting of 216 molecules in a cubic box, 8 water molecules were replaced by an equal number of urea molecules. In order to contrast with the dimer approximation (see below), the urea molecules were put at maximum distance from each other. After energy minimization the system was equilibrated during 30 ps, and a *NpT* production run of 50 ps. was performed.

### B. Urea dimer in solution

From the crystal structure, we took those two dimers which appeared to be energetically the most stable.<sup>11</sup> First, a linear dimer with collinear carbonyl groups [Fig. 1(a)] and second, a cyclic dimer consisting of monomers perpendicular to each other [Fig. 1(b)]. Both configurations were subjected to an MD simulation *in vacuo* to obtain the most stable structures. As a result, the linear dimer transformed into a "forked" dimer [Fig. 1(c)], also obtained by Cristinziano *et al.*<sup>18</sup> by energy minimization. The cyclic dimer remained cyclic but turned into a flat configuration [Fig. 1(d)], in accordance with Ref. 18. On subsequent careful equilibration in solution (described below), only the latter dimer appeared to remain stable. Therefore we performed full MD runs only for this dimer. For this purpose we constructed a cubic simulation box containing 4 dimers and 208 D<sub>2</sub>O molecules. After energy minimization, we performed a 20 ps *NVT* equilibration run of the water structure around the dimer, keeping the urea coordinates fixed. Next, *NpT* equilibration of the whole system was performed, allowing the dimer to adjust slowly to the water temperature and structure. After this "careful treatment," a subsequent production run of 50 ps was performed.

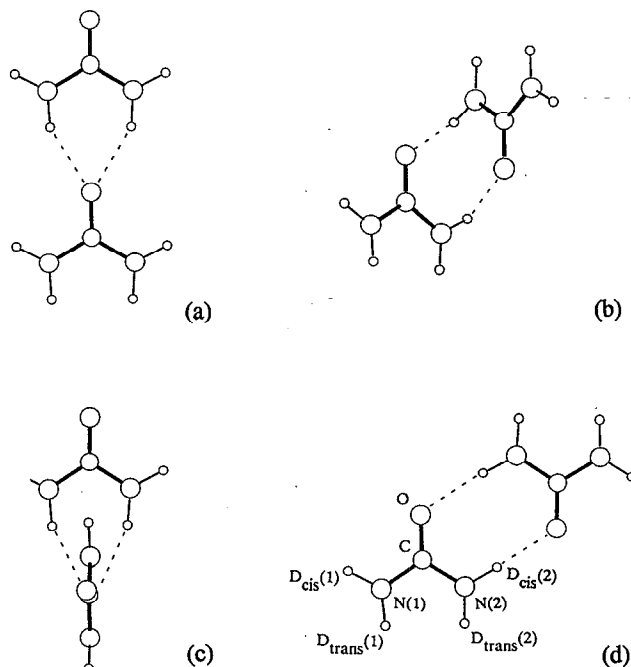


FIG. 1. (a) Linear urea dimer from the crystal structure. (b) Cyclic urea dimer from the crystal structure. (c) Forked urea dimer obtained from simulation *in vacuo*. (d) Cyclic urea dimer obtained from simulation *in vacuo*.

In order to investigate the size of the simulation box, and to see whether the dimer might be stabilized by the surrounding water molecules in the dilute limit, we decided to perform a simulation with 50 D<sub>2</sub>O molecules and only one cyclic dimer in a truncated octahedron. After applying the same careful treatment as mentioned above, i.e., *NVT* equilibration with the dimer kept fixed followed by 10 ps of *NpT* equilibration, a 100 ps production run was performed. Because it turned out that the truncated octahedral boundary conditions might have induced a freezing of the liquid, the simulation was repeated using a cubic box.

For a complete survey of the simulation details we refer to Table I.

## III. SIMULATION RESULTS

### A. Solution structure

The structure of the urea solution can be examined in terms of atom-atom pair correlation functions  $g_{\alpha\beta}(r)$ . The direct interactions between urea and water were analyzed from pair correlation functions between water oxygen ( $O_W$ ) and urea oxygen ( $O_U$ ) and deuterium, respectively. The deuterium atoms are distinguished as *cis* and *trans* deuterium ( $D_{cis}$  and  $D_{trans}$ , respectively), referring to the position relative to the carbonyl group, [see Fig. 1(d)]. The radial distribution functions, which are presented in Fig. 2, all display a clear first hydration shell. Moreover, the monomer and dimer correlation functions in the cubic boxes are very much alike, indicating that the results are independent of system size and starting configuration (the truncated octahedron is not considered here for reasons

TABLE I. Simulation details.

	Monomer		Dimer	
	Cubic	Truncated octahedron	Cubic	Cubic
Periodic boundary conditions	Cubic	Truncated octahedron	Cubic	Cubic
No. of urea monomers	8	...	...	...
No. of urea dimers	...	1	1	4
No. of water molecules	208	50	50	208
Box dimensions (Å)	19.06	15.16	12.47	19.09
Cutoff radius (Å)	8.5	7.5	6.0	8.5
$\tau_T$ (ps)	0.1	0.1–0.05	0.1–0.05	0.1
$\tau_P$ (ps)	0.5	0.5–0.25	0.5–0.25	0.5
$\beta_T$ ( $10^{-10}$ Pa)	4.02	4.02	4.02	4.02
Storage of coordinates ( $\text{ps}^{-1}$ )	0.05	0.02	0.02	0.05
Storage of energies ( $\text{ps}^{-1}$ )	0.02	0.02	0.02	0.02
$NVT$ equilibration (ps)	...	20	20	20
$NpT$ equilibration (ps)	30	10	10	10
$NpT$ production (ps)	50	100	100	50
Temperature (K)	299	304	308	299

given below). In general, all features are in good agreement with previous simulations.<sup>7,10</sup> The number of water molecules around  $\text{O}_U$ , obtained by integrating the pair correlation function for  $\text{O}_U\text{--O}_W$  until the first minimum, is equal to 2.8 for the monomer simulation. In the same way we find 1.6 water molecules around the urea deuterium atoms, equally distributed among  $D_{cis}$  and  $D_{trans}$ . Since there is no overlap between these groups, this means that about 4.4 water molecules are present in the first solvation shell of urea. This compares reasonably to the calorimetric value of five<sup>19</sup> while Åstrand *et al.*<sup>10</sup> have found 5.7 neighbors. From all this we may conclude that the simple urea–water pair potential we used is good enough to describe the local solvation behavior of urea.

In Fig. 3 the water–water oxygen radial distribution functions  $g_{\text{OO}}(r)$  are shown for solvent water in the different urea solutions and for pure water. The pair correlation functions for the monomer and dimer simulations in the cubic boxes are practically indistinguishable from the one for pure water (only the first maxima are a bit higher). This means that probably the bulk water structure is not very much affected by the presence of urea in the solution. This is in agreement with Åstrand *et al.*<sup>10</sup> and does not support the FF structure breaking model, from which we would have expected an inward shift of all the peaks. Of course, long range angular correlations between two water molecules in urea solutions may still be different from those in pure water.

Performing the same calculations for the small truncated octahedron, we noticed some peculiarities, concerning much stronger correlations in the  $g_{\text{OO}}(r)$  than in the other boxes. In order to check this point, we performed a test simulation of a pure water box with the same small size and truncated octahedral periodic boundary conditions. It was found that the water was completely “frozen” into a cubic latticelike structure. This “crystallization” phenomenon does not occur in larger truncated octahedral boxes nor in small cubic systems. Therefore, we conclude that this is an artefact, introduced by the combination of the small system size and periodic boundary conditions, and that the results of Ref. 8 should be doubted.

## B. Dimer stability

In Sec. II we described the careful equilibration, necessary to obtain a sufficiently stable dimer in solution. From this it may already be inferred that the cyclic urea dimer would not be stable under normal conditions in real two molal urea solutions. A more detailed picture of the dimer stability can be obtained from an analysis of the intermolecular urea–urea atom pair correlation function of  $D_{cis}$  and  $D_{trans}$  on the one molecule around  $\text{O}_U$  on the other one [see Fig. 1(d)]. Although the results obtained from the small truncated octahedral box are probably unreliable, the fact that the cyclic dimer remains stable in this box makes it a good reference case for the discussion of the results of the cubic boxes. Therefore, we will discuss this case first. The  $D_{cis}$  radial distribution function for the single dimer in a truncated octahedron [Fig. 4(a)] is in good agreement with Ref. 8: the peak at 2 Å represents a single  $\text{O}_U\text{--}D_{cis}$  bond while the peak at 3 Å indicates that the other  $\text{O}_U\text{--}D_{cis}$  bond has fallen apart. The peak at 5 Å represents the distance between  $\text{O}_U$  and the second  $D_{cis}$  which does not form a bond. The coordination number is about 0.5 for both first and second peak and 1 for the third peak, which means that, averaged in time, one  $\text{O}_U\text{--}D_{cis}$  bond remains stable. As we already noticed, however, this stability is probably imposed by the size and symmetry of the truncated octahedral simulation box. This is confirmed by the correlation functions obtained from the dimer simulations in both cubic boxes, which show much less correlation [Fig. 4(b)]. Although the dimer radial distribution functions are somewhat different from the monomer function (a relict of the dimer can be observed from the first peak at 2 Å), we can conclude that the dimers break up totally in two molal aqueous urea solutions. This conclusion is confirmed by the  $D_{trans}\text{--O}_U$  pair correlation function of the cubic boxes (not presented), showing that also  $D_{trans}$  is accessible to  $\text{O}_U$ . In order to check the long-term behavior, a 1000 ps run of the small cubic box was performed. The solute–solute interaction energy of the urea molecules remained constant close to zero over the whole time range, indicating that no dimer formation has occurred. The resulting

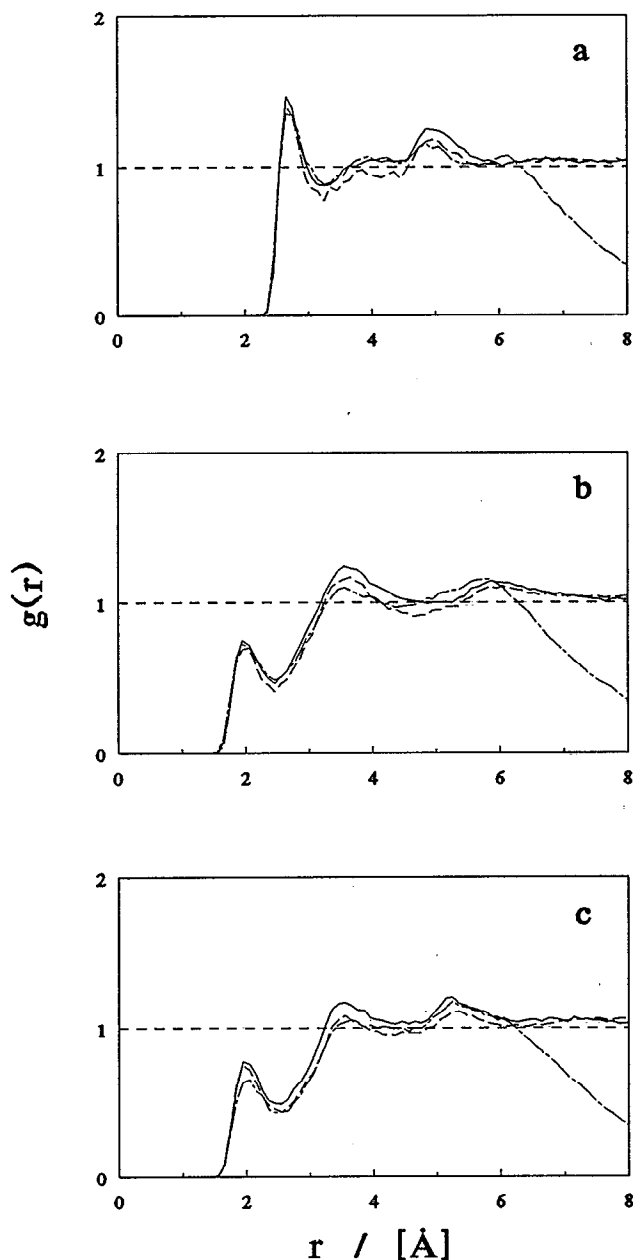


FIG. 2. Urea-water radial distribution functions for eight monomers in cubic box (drawn line), four dimers in cubic box (dashed line) and one dimer in cubic box (dash-dot line: distorted beyond the half-box length of 6 Å) for water oxygen ( $O_W$ ) relative to (a) urea-oxygen ( $O_U$ ); (b) urea-*cis* deuterium ( $D_{cis}$ ); (c) urea-*trans* deuterium ( $D_{trans}$ ).

$O_U$ - $D_{cis}$  distribution function [Fig. 4(b)] shows a gradual transition to the monomer case, as might be expected.

### C. Total nitrogen radial distribution function

In order to compare the simulation results with neutron scattering experiments,<sup>9</sup> the nitrogen-centered radial distribution function  $G_N(r)$  was calculated from the weighted sum of the partial pair correlation functions involving nitrogen,  $g_{N\alpha}(r)$ , according to

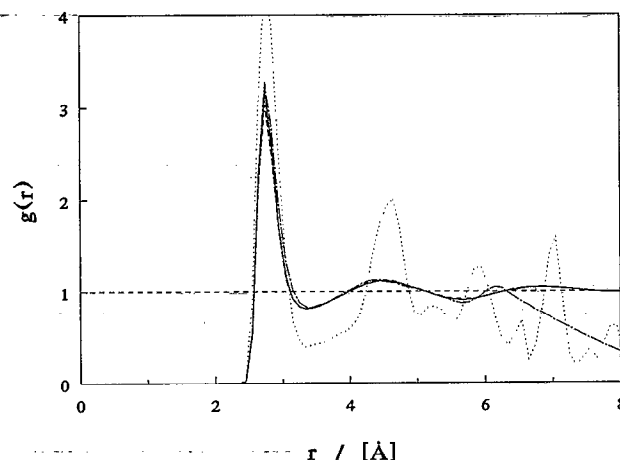


FIG. 3. Water-water radial distribution functions:  $g_{OO}(r)$  for pure water (long-dashed line), eight monomers in cubic box (drawn line), four dimers in cubic box (short-dashed line), one dimer in cubic box (dash-dot line), one dimer in truncated octahedron (dotted line). The last two functions are distorted beyond the half box length of 6 and 7.5 Å, respectively.

$$G_N(r) = \sum_{\alpha} c_N c_{\alpha} b_N b_{\alpha} g_{N\alpha}(r),$$

where  $c_{\alpha}$ ,  $b_{\alpha}$  are the atomic fractions and neutron scattering lengths<sup>20</sup> respectively, and  $\alpha$  runs over all types of atoms in both urea (i.e., N, C,  $O_U$ , and  $D_U$ ) and  $D_2O$  (i.e.,  $O_W$  and  $D_W$ ).  $b_N$  is the difference between the neutron scattering lengths of the two nitrogen isotopes. The  $g_{N\alpha}(r)$ 's include both intra- and intermolecular correlation functions. The region beyond 2 Å, where intermolecular correlations turn up, is shown in Fig. 5 for the three cube simulations (the truncated octahedral simulation is omitted from now on). Nevertheless, in this region some intramolecular peaks are present: the first big peak at 2.25 Å arises from the urea intramolecular N-O, N(1)-N(2) and N(1)- $D_{trans}(2)$  correlations, while the second one at 3.2 Å is caused by intramolecular N(1)- $D_{cis}(2)$  correlations. When we consider only the intermolecular part now,  $G_N(r)$  is quite smooth and structureless, and has a maximum at 3.45 Å, comparing reasonably well to previous work.<sup>9,10</sup> The experimental  $G_N(r)$ , however, shows stronger oscillations than our simulated ones. According to the authors<sup>9</sup> this should be a real feature and not be due to truncation ripples. In order to investigate this point, a Fourier transformation of our  $G_N(r)$  was performed up to  $r_{\max} = 8.5$  Å (respectively, 5.0 Å for the small cubic box), after subtraction of a constant term  $G_N(r=r_{\max})$  in order to put the tail of  $G_N(r)$  on zero

$$\Delta_N(k) = 4\pi\rho \int_0^{r_{\max}} dr r^2 \frac{\sin(kr)}{kr} G_N(r),$$

where  $\rho$  represents the particle density, i.e., the number of particles per unit volume. The simulated scattering function  $\Delta_N(k)$ , which is presented in Fig. 6 for the monomer case, shows a reasonable agreement with the experimental function of Finney and Turner. Then  $\Delta_N(k)$  was transformed back to  $\bar{G}_N(r)$  by a Fourier integral up to the experimental truncation point of  $k_{\max} = 16 \text{ Å}^{-1}$

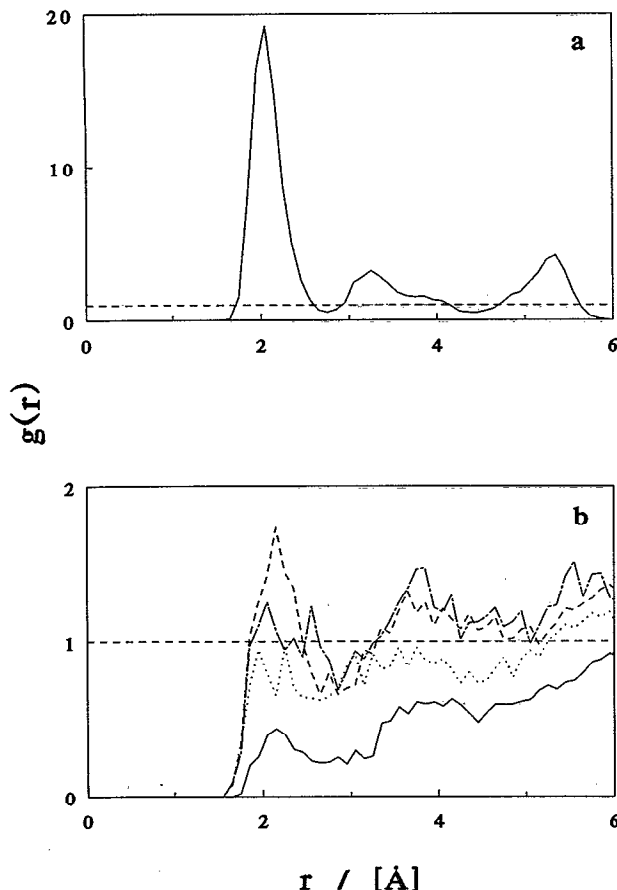


FIG. 4. Urea-urea intermolecular radial distribution functions for oxygen ( $O_U$ ) on the one molecule relative to *cis* deuterium ( $D_{cis}$ ) on the other molecule for (a) one dimer in truncated octahedron; (b) eight monomers in cubic box (drawn line); four dimers in cubic box (dashed line); one dimer in cubic box, 100 ps run (dash-dot line). One dimer in cubic box, 1000 ps run (dotted line).

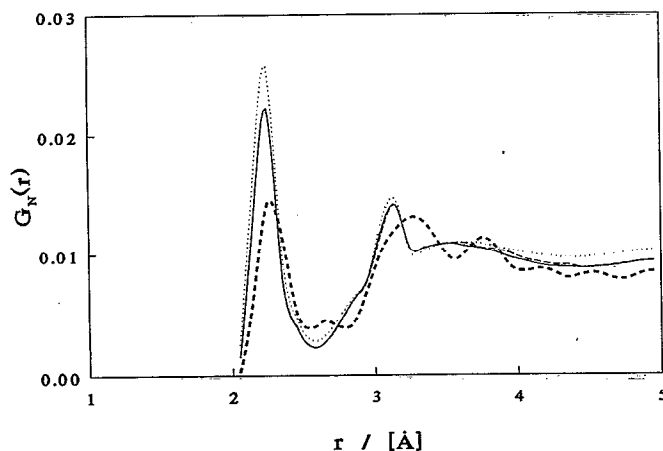


FIG. 5. The nitrogen-centered  $G_N(r)$  beyond 2 Å for 2 molal urea in  $D_2O$  before Fourier transformation for eight monomers in cubic box (drawn line); four dimers in cubic box (dashed line); one dimer in cubic box (dotted line); experimental  $G_N(r)$  from Ref. 8 (fat-dashed line).

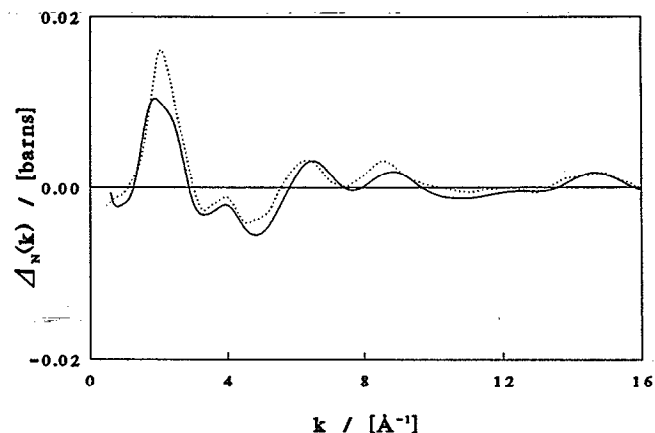


FIG. 6.  $\Delta_N(k)$  for two molal urea in  $D_2O$ : experimental first-order difference  $\Delta_N(k)$ , redrawn from Finney and Turner (Ref. 9) (dotted line); eight monomers in cubic box (drawn line).

$$\bar{G}_N(r) = \frac{1}{2\rho\pi^2} \int_0^{k_{\max}} dk k^2 \frac{\sin(kr)}{kr} \Delta_N(k).$$

The transformed  $\bar{G}_N(r)$  for the monomer simulation, to which the constant term  $G_N(r=r_{\max})$  is added again, is shown in Fig. 7 together with the experimental region beyond 2 Å. The Fourier transformation back and forth indeed produces additional oscillatory structure, corresponding to the experimentally observed truncation ripples. The small peak in the experimental distribution at 2.7 Å is reproduced by our simulation, but only after Fourier transformation back and forth. This means that this peak has no physical meaning, but should be interpreted as a truncation ripple. We have checked that our method is insensitive to changes in the truncation point  $r_{\max}$ . We want to stress here that the truncation ripples do not appear if the intramolecular correlations are left aside.

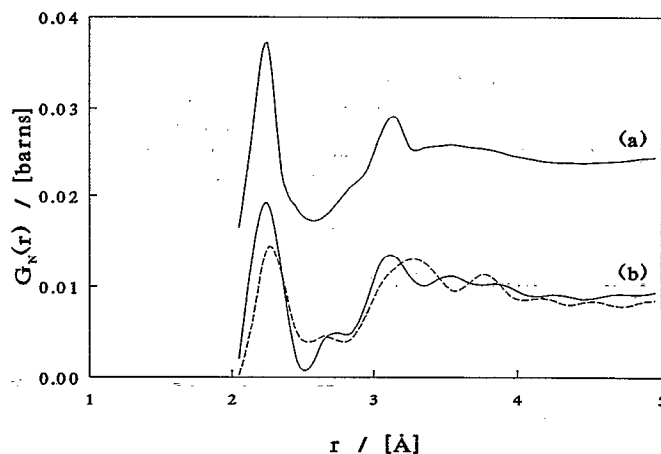


FIG. 7. The nitrogen-centered  $G_N(r)$  beyond 2 Å for two molal urea in  $D_2O$  for eight monomers in the cubic box: (a)  $G_N(r)$  before Fourier transformation. The plot has been translated by 0.015 units on the  $y$  axis for clarity. (b)  $\bar{G}_N(r)$  after Fourier transformation (drawn line) compared to the experimental  $G_N(r)$  (dashed line).

Although the height of the first peak and the position of the next peaks are somewhat different from those in the experimental curve, our potential model and Fourier transformation procedure reproduce the experimental results reasonably well. It seems reasonable to expect that a small enlargement of the intramolecular bond lengths might shift the second peak in the direction of the experimental one.

#### IV. DISCUSSION AND CONCLUSIONS

Molecular dynamics simulations of two molal deuterated urea solutions in D<sub>2</sub>O have been performed. In order to investigate the stability of the cyclic urea dimer in aqueous solution, simulations were performed using urea monomer and dimer starting configurations in computational boxes with various sizes and periodic boundary conditions. Only the cyclic dimer appeared to be stable enough to survive a careful equilibration procedure. Nevertheless, in the subsequent production runs also this dimer gradually fell apart. We conclude therefore that the existence of urea dimers in two molal urea solutions is very improbable. We have shown that the partial stability of the cyclic dimer in a truncated octahedron, as obtained by Cristinziano *et al.*<sup>8</sup> is an artifact of the limited size and imposed symmetry of that box. Therefore we consider this phenomenon not to be of physical importance.

A comparison with neutron scattering experiments has been made by calculating the total nitrogen radial distribution function  $G_N(r)$ . The calculated function is in reasonable agreement with the experimental function, when both intra- and intermolecular correlations are taken into account and the experimental truncation ripples are introduced by a Fourier transformation of  $G_N(r)$  back and forth. Comparing the intermolecular parts of  $G_N(r)$  only, we suspect that some of the potential functions used in previous simulations<sup>9,10</sup> might also be adequate to reproduce the experimental  $G_N(r)$ . Contrary to the remark of

Finney and Turner,<sup>9</sup> we think that  $G_N(r)$  does not provide a very severe test of the potential.

From these results, combined with the good agreement with Åstrand *et al.*<sup>10</sup> concerning the local solution structure, we conclude that our potential function is sufficiently adequate to model the urea-water interactions.

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